The Oxidation of Olefins and Paraffins
In Low Temperature Fuel Cells

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We concluded that a low temperature hydrocarbon fuel cell might be feasible when we found that current could be drawn from an ethylene or propane depolarized platinized porous carbon electrode for a sustained period at 80°C and that under these conditions the hydrocarbon was completely oxidized.[1] Similar results with these and some other hydrocarbons have since been reported from other laboratories.[2,3]

Further studies of the behavior of hydrocarbons on platinized porous carbon electrodes in aqueous sulfuric acid electrolytes are discussed in this paper. Results from rotating disk and small platinum foil electrodes have been reported by other members of our group.[4]

We chose to use platinized porous carbon electrodes for hydrocarbon product studies in order to make enough product for quantitative determination. Porous carbon and graphite are electrically conducting, resistant to acidic and basic electrolytes, and are available in a variety of porosities and surface areas. Further modification by chemical treatment is also possible.

The use of porous electrodes for electrochemical measurements and for electrocatalyst studies does result in some problems. These difficulties are shared by those working with "practical" fuel cell electrodes. The theory of porous electrodes is inadequate at present. However, it is receiving much attention because it is probable that the practical fuel cell electrodes will be porous structures. This is necessary if large electrocatalyst surface areas and high fuel cell power densities are to be attained.

Time-dependent polarization leading to unstable current-potential behavior complicates the use of current-potential measurements in the evaluation of porous electrodes which are depolarized with saturated hydrocarbons. These difficulties can be avoided by using pseudo steady-state currents after step changes in electrode potential. This procedure gives current-potential curves similar to those obtainable by potential-sweep methods with small electrodes and shows promise for use in the detailed comparison of very different electrodes and systems. From these curves, large differences in behavior of olefins and paraffins can be seen. It is clear that the unstable current-potential behavior with paraffins at high constant currents is not due to inadequate mass transfer immediately adjacent to the electrode but rather to the lower currents that can be supported by paraffins as the electrode potential is polarized above peak current potentials. Electrode poisoning occurs in this potential region with the formation of an oxide film on the electrode. This could inhibit adsorption of the paraffins and reduce the number of

effective catalyst sites for the paraffin oxidation. The potential at which this effect will dominate over the tendency for the current to increase with increasing potential differs with different fuels and probably depends on their ability to inhibit formation of the oxide film or to remove it as it is formed. With olefins, the potential of peak current is more positive than that of an oxygen counterelectrode.

Hydrocarbon depolarized electrodes were also found to be much more sensitive to inhibiting influences than electrodes depolarized with more reactive fuels. Different types of inhibition by air and oxygen and by extreme polarization of a fuel cell anode were observed and interpreted. When carbon monoxide was injected into the feed stream to a propane or propylene depolarized electrode, an improvement of performance resulted. No effect was evident when carbon dioxide was injected in this way. Preliminary experiments were made to evaluate the possibility of using inhibition data in the study of porous electrode activity and behavior. However, the factors affecting the shape and size of these inhibition peaks are complex; and more study will be required before they are completely understood or before significant application of these techniques can be expected.

Apparatus and Methods

1. Product Studies

The apparatus used for our new hydrocarbon product studies is shown in Figure 1. It differs slightly from that described before.[1] Fritted-glass separators fused in place are used instead of ion exchange membranes to separate the three cell compartments. A means of equalizing pressure is provided to minimize flow of electrolyte from one compartment to another. The Ascarite "carbon dioxide" absorption tube is preceded by a condensate trap, Drierite and Anhydrone, to remove sulfuric acid spray and water. Ascarite and Drierite follow the Ascarite "carbon dioxide" absorption tube to exclude moisture and atmospheric carbon dioxide.

The apparatus was thoroughly flushed with the hydrocarbon used before weighing the Ascarite tube at the beginning of each experiment. At the end of an experiment, hydrocarbon flow was continued until at least 2 liters of gas passed through the anode in order to remove all carbon dioxide product from the cell. Additional flushing for an equal period gave changes in the weight of the Ascarite tube of the order of $\pm$ 0.5 mg.

Constant cell currents were maintained by automatically varying the load resistance as was previously described.

Current and anode potential versus SCE at 25°C were recorded on a calibrated dual-pen Varian recorder. The reference electrode was a Beckman saturated calomel electrode maintained at room temperature (25°C) and connected to a Luggin capillary through a long, small-diameter bridge filled with the fuel cell electrolyte. The anode potential versus the saturated calomel electrode (SCE) was sensed by a Keithley Model 600A electrometer with recorder output. Potentials in this paper are reported versus NHE with the sign of the oxygen electrode positive relative to the hydrogen electrode.

2. Potential-Step Voltammetry

In its simplest form the apparatus used for potential-step voltammetry consisted of a cell like that used for the product studies but modified for half-cell studies by substituting a platinum gauze cathode for the oxygen electrode. Current through the cell was provided by a storage battery in series with variable resistors. Anode potential was controlled by manually adjusting these resistors. Current and potential were sensed and simultaneously recorded as previously described.

Recently we have used one function of a versatile two-stage constant potential/constant current d.c. power source in place of the manually controlled system. The preregulator uses a magnetic amplifier and controlled rectifiers. The second regulator stage uses power transistors with an adjustable gain amplifier for control.

In the constant potential mode, the potential difference between the fuel cell anode and a reference electrode is sensed by an electrometer amplifier. The output of this is compared with an adjustable reference voltage. The difference is then used, through an operational amplifier, to maintain the anode at constant potential.

Slow response of the fuel cell anode potential with changes in cell current requires time delay circuits to limit the rate of change of the power supply output. This is accomplished through variable capacitor feedback to the operational amplifier which controls the power to the test cell.

3. Air and Oxygen Inhibition Experiments

The apparatus used was similar to that for potential-step voltammetry. Current was supplied to the cell from a storage battery through variable resistors. Control circuits provided for automatic constant current operation.

Inhibition data were obtained by injecting 2.48-ml portions of air, oxygen, and other gases into the fuel gas stream before it passed through a platinized porous carbon anode. This was done by means of a Wilkins XA-202 gas sampling valve.* Propane and propylene were each used as fuels. Flow rates were measured on the exit gas from the anode compartment using a soap film flowmeter.

4. Electrodes

The electrodes used were similar in form to those previously described.[1] Each consists of a porous carbon cylinder 2-1/2 inches long, 3/4-inch OD, and 1/2-inch ID which is fitted tightly to a 1/2-inch OD impervious graphite tube. This tube serves as electrical conductor and gas conduit. The lower end of the cylinder is closed with a graphite plug, and the joints are sealed with an Epon resin.**

 * Wilkins Instrument and Research, Inc.,
     P.O. Box 313, Walnut Creek, California.

** Epon 828-2, Shell Chemical Company.

As used in the experiments described here, the electrodes were sometimes new; in other cases they had been used extensively with various fuels and electrolytes at different conditions.

The platinum was applied to the electrode by two general methods:

Method A

The electrode was electroplated for 20 minutes at ambient temperature and at a current density of 40 ma/cm^2 in a 1.25- or 1.5-inch diameter graphite cup which served as the counter electrode. The plating solution was drawn into and forced out of the electrode every 2 minutes during the plating period. Sometimes this procedure was repeated. Different plating solutions were used as shown in Table I.

More active electrodes were obtained by Method B:

Method B

The porous carbon electrode blank was impregnated with chloroplatinic acid solution containing 10 weight per cent platinum. It was dried on a rotating graphite mandrel in an air oven at 140°C and was reduced for 3 hours in a stream of hydrogen at 400°C. It was then mounted and sealed.

The preparation and geometric areas of the electrodes are summarized in Table I.

New Product Studies

Product data which we reported previously[1] showed that ethylene and propane can be completely oxidized in fuel cells at 80°C. New data for propane reconfirm this result, but data from n-butane suggest that incomplete oxidation of this hydrocarbon can occur under some conditions that give complete oxidation with propane.

The new results were obtained using a platinized porous carbon electrode (Electrode A, Table I) with sulfuric acid at 80°C. In this series, the cell was operated at 25.2 ma (0.84 ma/cm^2). A slow decrease in cell voltage occurred with time. When the cell voltage dropped close to the point where the current could no longer be maintained, a short period at open circuit restored the electrode activity for further operation under load. Initial anode potentials for propane and n-butane under load were of the order of 0.45-0.50 volt (versus NHE) increasing with time to 0.74-0.84 volt.

The present series consisted of two propane experiments followed by three n-butane experiments and another propane experiment. The product results are summarized in Table II.

The "carbon dioxide" values for n-butane are 6-8% above theory based on the ampere-hours produced during the experiments. This excess could come from direct chemical oxidation of n-butane by oxygen transported through the electrolyte from the cathode chamber or from some electrooxidation of the electrode carbon. This would give more carbon dioxide per coulomb than can be obtained from a hydrocarbon. However, similar oxygen transport or carbon oxidation would

be expected in the propane experiments which gave the theoretical amount of "carbon dioxide." Partial oxidation products absorbed from the fuel cell exit gas stream with the carbon dioxide could also account for a high "carbon dioxide" value. Calculations were made for Experiment No. 4 (Table II) which gave 108.2% of the theoretical amount of "carbon dioxide." Cases were considered where the partial oxidation product was butanol, butanone, butyric acid, or acetic acid. Assuming complete recovery of the products, values of 9 to 14 weight per cent of partially oxidized n-butane in the "carbon dioxide" product were calculated. As it is improbable that all of the partially oxidized materials reached and were retained in the Ascarite tube, even higher percentages of partially oxidized products are possible.

The Evaluation of Hydrocarbon
Depolarized Electrodes

As part of a program to improve the performance of platinized porous carbon electrodes, propane was chosen as a test material. With this hydrocarbon we had considerable difficulty in using conventional potential-current plots because of time-dependent polarization.

The nature of these difficulties can be seen more clearly from curves showing the change in electrode potential with time at constant current. This is illustrated in Figure 2. Here the over-all cell voltage is plotted against time. Sequence numbers and current are shown on each curve. Curves 1 and 2 were both recorded at 10 ma current and show the effect of the removal of active products from preelectrochemical reactions. Curve 6, also at this current, may illustrate further removal of active materials or the formation of inhibitors during the intermediate experiments. The rapid decrease in potential at the end of the 100-ma curve is characteristic of time-potential curves at higher currents and would be accentuated at still higher currents.

Another example of the effect of preelectrochemical reactions on time-dependent polarization is seen in Figure 3. Here an attempt to remove impurities and intermediates from an electrode was made by use of a repetitive test cycle. The anode was caused to cycle from 0.44 to 0.84 volt under load with return from 0.84 to 0.44 volt at open circuit. In the course of several cycles, it was expected that impurities would be removed and reproducible cycles obtained. In practice, variations in treatment of the electrode immediately before test caused more change in the first few cycles than later; but a continuing decrease in polarization time and increase in recovery time occurred as each series progressed. Preliminary tests were made in order to select appropriate current ranges for each cycle test series. The curves in Figure 4 are derived from these data. The upper curve represents the time in minutes for the anode to polarize from 0.44 to 0.84 volt plotted against the number of test cycles. The lower curve shows the corresponding data for recovery times from 0.84 to 0.44 volt.

Data like these were used by us in some cases for comparing electrodes or for investigating the effects of pretreatments on the behavior of a particular electrode.

Potential-Step Voltammetry

In an effort to simplify the interpretation of electrochemical

data from porous electrodes, we attempted to establish steady-state conditions by prolonged operation of bubbling hydrocarbon depolarized electrodes at a series of fixed potentials.

If no change in the catalytic activity of a fuel cell anode occurs, it should be possible to establish a steady-state current at constant potential for each set of conditions. In this situation current would be determined by the catalytic activity of the electrode surface and the steady state concentrations of reactants and products at the electrode surface.

With our platinized porous-carbon anodes depolarized with propane, this steady state is not reached in 4 hours at 80°C at 0.74 volt; though in many cases the current was decreasing very slowly at this time. A curve obtained using automatic potential control is shown in Figure 5.

Many experiments were carried out to determine the reproducibility of constant potential-current data and to provide a basis for selecting test sequences which would give satisfactory, comparable data in the least time. These curves appear to consist of two sections. In the first part, the current is changing rapidly. This section of the curve appears to be affected considerably by recent electrode history and is sometimes difficult to reproduce. After a period which varies in length, depending on the recent history of the electrode, a steady state is approached. With some fuels, such as ethylene and propylene, the current will remain constant for long periods; with others, such as propane, a gradual, slow decline in current is observed. With the electrodes listed in Table I, 20 to 60 minutes was ordinarily used at each controlled anode potential.

Fuel Cell Oxidation of Propane,
Isobutane, Propylene, Ethylene,
and Hydrogen in 5 N H_2SO_4 at 80°C

The anode current densities corresponding to different anode potentials were measured by a constant-potential technique for propane, isobutane, and propylene. These data are shown in Figure 6. The points shown correspond to current densities 20 minutes after the indicated potential was established. A current-potential curve for hydrogen on this electrode is included for reference.

Curves showing ethylene and propylene performances are plotted in Figure 7. These data were taken from constant-current experiments, but in these cases the rates of polarization with time were so slow that the data actually were obtained at nearly constant potentials. The ethylene curve is similar to the propylene curve but is displaced slightly toward more favorable lower anode potentials.

The shapes of the propane and propylene curves correspond fairly closely with potential-sweep data obtained using a platinum-foil electrode and 2 N sulfuric acid electrolyte. These data are plotted in Figure 8.

From Figure 6 it is seen that with the saturated hydrocarbons, propane and isobutane, the anode current increases to a maximum between 0.6 to 0.7 volt and then decreases as the anode is polarized further. This type of behavior appears to be general for

saturated hydrocarbons. It is also found with saturated hydrocarbons that at anode potentials above those for maximum current, the rate of decay of current increases as the anode potential increases; and "steady-state" currents require more time to establish. Up to a point it is possible to draw more current temporarily by decreasing the load resistance but at the expense of rapidly increasing polarization. Thus, with the constant-current methods ordinarily used in determining electrode current-dependent polarization, a "limiting" current is found beyond which unstable electrode behavior is observed.

Olefins differ from paraffins in their current-potential behavior (Figures 6, 7). They give higher "steady-state" currents as the potential is increased beyond the region of interest for hydrocarbon-oxygen fuel cells. Therefore, they do not give the "limiting" currents found with saturated hydrocarbons.

Air and Oxygen Inhibition of Hydrocarbon-Depolarized Electrodes

The study of hydrocarbon-depolarized electrodes is complicated by their susceptibility to various inhibiting influences. Such effects were much less apparent with hydrogen, methanol, and other more active fuels.

Inhibition by air or oxygen is one such effect. It is also one of practical interest as there is always some possibility that air or oxygen may contact a fuel cell anode.

Typical inhibition behavior is observed when a little air enters the feed line to a hydrocarbon fuel cell anode. A severe polarization occurs resulting in a very sharp increase in anode potential. This change in potential can amount to several tenths of a volt, and the electrode potential can approach that of an oxygen cathode.* Recovery of the original anode potential may require a minute or two or several minutes, depending on the hydrocarbon involved, the amount of air admitted, and the temperature.

Variable "induction" periods which often occur on startup with saturated hydrocarbons are also probably due to air inhibition. Examples with propane are shown in Figure 9. Curves 1 and 2 were obtained on successive days with Electrode A (Table I). The exposure to air differed, and Curve 1 shows less inhibition than Curve 2. In other cases "induction" periods from a few minutes to several hours have been observed. All of the curves show a gradual initial drop in potential followed by a rapid transition to a potential minimum and then a gradual increase to a constant open-circuit potential. These open-circuit potentials, although reasonably constant in a particular experiment, do vary a little from one experiment to another.

Similar behavior is noted when enough oxygen is injected into the propane stream to bring the potential of the electrode above 0.8 volt. Inhibition curves obtained with Electrode F (Table I)

* In our equipment, open-circuit potentials of 1.058 to 1.081 volt were observed with platinized porous carbon electrodes at 80°C in 5 N sulfuric acid electrolyte with oxygen at 1 atmosphere pressure. Lower potentials are, of course, obtained under load.

resulting from the injection of different amounts of oxygen are shown
in Figure 10. Here the transitions are less abrupt than those in
Figure 9. The electrodes are quite different, but there may also be
some differences in the nature of the inhibition.

Polarization of a propane-depolarized platinized porous
carbon electrode under load until potentials above approximately 0.94
volt are attained also inhibits the electrode. Operation at open cir-
cuit then gives a gradual initial drop in potential followed by a
rapid transition to open-circuit potential. The effect of the elec-
trode potential on the potential recovery curves at open circuit for
Electrode G (Table I) is shown in Figure 11. In these experiments the
cell was operated at 100 ma current until the anode polarized to the
test potential. The current was then manually adjusted as required to
hold this potential for 7 minutes. The circuit was then opened, and
the potential recovery curve was recorded. The single exception to
this is the highest potential case. Here the circuit was opened as
soon as the 1.14-volt potential was reached.

A slight convex shape of the recovery curve is seen after
operation at potentials as low as 0.64 volt. Pronounced effects,
however, are not observed until 0.94 volt or more is reached.

The possibility that hydrocarbon fuel cell anodes can be
inhibited by polarization may be of practical concern. With present
oxygen-propane fuel cells, anode recovery at open circuit is rapid
even after brief short circuit because the potential of the anode
cannot exceed the relatively low potential of the polarized oxygen
counterelectrode. However, if oxygen electrode efficiencies are
improved, their potentials could be high enough to substantially
inhibit some saturated hydrocarbon depolarized anodes. These poten-
tials can also be attained in a multiple fuel cell arrangement or in a
fuel cell where the anode half cell is coupled with a halogen-
depolarized electrode or other high potential system.

The inhibited electrode is restored by contact with propane
in due time. The activity toward propane can also be restored rapidly
by injecting small amounts of more reactive fuels into the propane
stream. Reactivation of Electrode F (Table I), which had been polar-
ized under load, can be seen in Figure 12. Here hydrogen was used as
the reactive fuel.

The experiments described in the following section were
carried out to obtain more information about the characteristics and
the nature of the air and oxygen inhibition. In this series some
factors were maintained constant. The same seasoned electrode
(Electrode D, Table I) was used in all experiments. The air or oxygen
volume injected into the hydrocarbon feed stream was 2.48 ml in each
case. The electrolyte was nominally 5 N sulfuric acid. It was
changed at intervals, but some variation in concentration occurred
because of evaporation of water by the gases passing through the anode
compartment.

Variables studied are temperature (40-80°C), hydrocarbon
fuel (propane, propylene), hydrocarbon flow rate (5-15 ml/min), oxygen
content of the injected inhibiting gas (air, oxygen), anode current
(including open-circuit studies), and anode potential at the time of
injection of the inhibiting gas.

Temperature Effects

The effect of temperature on the inhibition of propane-depolarized anodes was studied by repeated injections of air into the propane feed stream at 40°C, 60°C, and 80°C at flow rates of 5, 10, and 15 ml/min. Single representative curves are shown in Figure 13. These data show that the rate of inhibition is so rapid that any effects of temperature are masked by other factors which control the shape of the ascending inhibition part of the anode potential curve. The slightly slower increase of the 40°C curve suggests that inhibition may be more rapid at higher temperatures, but this observed difference is within the limits of experimental error. The inhibition peak potentials are close to the same value in these series. The height and shape of the peaks do differ, however, with different electrodes and with changing activity of the same electrode.

After the initial break, the anode potential recovers logarithmically with half recovery at 8.0, 1.72, and 0.82 minutes at 40°C, 60°C, and 80°C, respectively.

 a. Effects of Hydrocarbon Flow
   Rate Through the Anode

The effects of hydrocarbon flow rate through the anode on the inhibition and recovery of propane anode potential were investigated at 40°C, 60°C, and 80°C. The data for the series at 80°C are typical and are shown in Figure 14. Comparable oxygen inhibition data for propane at 80°C are shown in Figure 15, while Figures 16 and 17 give corresponding curves for propylene.

One effect of the threefold increase in hydrocarbon flow rates in these experiments is to increase rate of inhibition of the electrode. The time from the beginning to maximum inhibition is very little more than the time required to sweep the air or oxygen into the electrode. The amount of inhibition in a given series was not affected by flow rate to any great extent. This is seen in the relatively constant height of the peaks in the anode potential curves. The greatest variations occurred in the experiments at the lowest flow rates. These were the first experiments in each series, and they were often carried out before the propane open-circuit potential had stabilized. The variations of this potential are seen at the extreme left on the curves. The recovery times, as well as the rates of the initial inhibition of the anode, are decreased by increasing the rate of hydrocarbon flow through the anode. Data illustrating this are plotted in Figure 18. These data were taken from curves such as those shown in Figures 14 to 17. A decrease in recovery time with increase in hydrocarbon rate is common to all of the experiments. The effect is less with propane than with propylene. Decreasing the temperature of a propane-depolarized anode from 80°C to 60°C slowed the recovery time after air poisoning. However, the two curves showing the recovery time, as a function of propane flow rates through the electrode, are parallel and show a comparatively small effect. Recovery times after poisoning with oxygen are much more dependent on the propane flow rate. This is most pronounced as the rate is increased from 5 to 10 ml/min.

 b. Effects of Load Current
   During Air Poisoning

The effects of operating a propane anode under load when air is injected are seen in Figure 19. These curves show the same rapid

response obtained at open circuit. The higher the anode potential at the time of air injection, the higher the inhibition peak. The incremental difference in peak height, however, is not linearly related to the difference in potentials at the time of injection. As the inhibition peak potentials increase, the recovery times also increase.

c. Effects of Oxygen Compared With Air and the Amount of Oxygen in Anode Poisoning

Direct comparisons of Figures 14 with 15 and 16 with 17 show the effects of substituting an equal volume of oxygen for air in poisoning a platinized porous carbon anode which is depolarized with propane or with propylene. In general, the peak heights in a given series are about the same. Even though peak heights are greater with oxygen, recovery times are only slightly longer than for air; and recovery time decreases more with increased hydrocarbon flow rate than is the case after air inhibition. The relative increase in the inhibition peaks for oxygen compared with air is less for propylene than for propane.

Other experiments carried out with Electrode F (Table I) show that the same peak heights are obtained if air or an amount of oxygen equal to that contained in the air is injected. The difference in peak heights with air and oxygen inhibition is due only to the fivefold difference in the amount of oxygen injected. Data showing the effects of amount of oxygen and air injected on the height of the inhibition peaks are plotted in Figure 20. The effect on the shape of the curves is seen in Figure 10. With this electrode, when the inhibition peak potentials get above 0.54 volt, there is a residual effect from one oxygen injection on the next. In a series of four injections of 4 ml of oxygen at 20-minute intervals, the peak potentials increased successively from 0.54 to 0.60 volt, even though the electrode potential returned to the same value between injections. The scatter of points in Figure 20 is due largely to such residual effects as the points were obtained at different times and in different sequence over a period of 3 days.

Discussion

1. Products from Hydrocarbon Oxidation

The new product work reported here confirms our earlier conclusion that propane can be completely oxidized in a fuel cell at 80°C. The n-butane data suggest, however, that hydrocarbon oxidation need not be complete and that higher molecular weight hydrocarbons may have a greater tendency to give isolatable intermediates. We have also observed odors tentatively identified as acetic acid and acetaldehyde from some ethylene "fuel cell" oxidations at potentials approximating those of the oxygen electrode. Such odors have also been reported by Young and Rozelle.[5]

Small amounts of side products would not be detectable by our analytical method, but we have ample electrochemical evidence for preelectrochemical reactions at open circuit with saturated hydrocarbons. We also see effects of a buildup of some inhibitors on our electrodes after prolonged experiments with various hydrocarbons. These can often be largely removed by drawing hot distilled water through the electrode, cleaning the cell, and using fresh electrolyte.

It is apparent that more product work should be done, especially at constant anode potentials and with some higher hydrocarbons. There appears to be a good chance of isolating intermediates which may provide clues to the hydrocarbon oxidation reaction mechanisms.

2. Oxygen Electrode Potentials

Although in this paper we are concerned mainly with the hydrocarbon fuel cell anode, oxygen and oxide films play an important part in inhibition behavior and in affecting hydrocarbon electrode performance at high polarizations.

The over-all oxygen half-cell reaction in acid is:

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O; E° = 1.229 \text{ volt.}$$

The equilibrium potential for this reaction can only be established on platinum when extreme care is used in preparing the electrode surface and in eliminating impurities from the test cell.[6,7] Usually, mixed potentials are obtained which give open-circuit voltages of the order of 1.06-1.09 volts versus NHE. In our equipment we have observed open-circuit potentials of 1.058-1.081 volt at 80°C in 5 N sulfuric acid. At the present state of development of the oxygen electrode in acid, therefore, there is an inherent loss of at least 0.18 volt before any current is drawn.

By present standards an oxygen electrode that will operate at 0.85 volt at 100 ma/cm² would be considered quite good. This corresponds to a 35% loss in efficiency due to the oxygen electrode alone in a hydrocarbon-oxygen fuel cell.

3. Hydrocarbon Electrode Potentials

Reaction potentials calculated from free energy changes for the complete oxidation of some hydrocarbons with oxygen are shown in the following table. Theoretical reversible half-cell potentials were calculated from thermodynamic data.

	Theoretical Reversible Potential for Complete Oxidation, Volts	Hydrocarbon Half-Cell Potential* Volt Versus NHE
Ethane	1.079	0.150
Ethylene	1.136	0.093
Propane	1.091	0.138
Propylene	1.127	0.102

* Calculated O_2 half-cell potential in acid, 1.229 volts vs NHE.

With ethane and propane the actual half-cell potential may go as low as or even lower than the calculated values. The actual processes occurring at the anode, however, are different from those represented by the theoretical reversible hydrocarbon half cells.

Thus, the saturated hydrocarbon potentials are probably determined largely by the concentration of hydrogen atoms resulting from dissociative adsorption of the hydrocarbons on the electrocatalyst. The open-circuit potentials observed with the olefins are always more positive than those from the paraffins. It may be that with olefins the adsorbed hydrogen atoms react to hydrogenate unsaturated species, giving paraffins which are then displaced by the more strongly adsorbed olefins.[2] During our air and oxygen inhibition experiments, when the feed to the electrode was changed from propane to propylene, the open-circuit potential gradually changed from about 0.29 volt to 0.50-0.55 volt. The reverse change occurred when propane was supplied to the electrode again.

Under load the polarization behavior of olefins and paraffins is very different. Even structures as closely related as ethane and propane can show large differences. This is revealed clearly by comparison of plots of pseudo steady-state current densities at constant potential versus potential (Figure 6). At low potentials the paraffins will often support higher currents than the olefins. With the paraffins, "steady-state" currents increase to maxima between 0.6 and 0.7 volt. This is well below the potential of an oxygen fuel cell cathode. With olefins, the current rises rapidly with potential beyond the fuel cell range. These differences are probably due to differences in the relative rates of reactions of paraffins and olefins at or with the oxide film on platinum. All electrodes are not alike in their detailed behavior, and we believe that pseudo steady-state current-potential curves should be valuable in more searching evaluations of electrodes, in studying the behavior of different fuels, and in determining the effects of operating variables.

The importance of oxygen and oxide films in determining the behavior of platinized porous carbon electrodes is also seen when inhibition behavior is considered.

4. Air and Oxygen Inhibition of Hydrocarbon Depolarized Electrodes

Three general types of inhibition of hydrocarbon depolarized porous carbon electrodes have been described in this paper. These are (1) inhibition of hydrocarbon oxidation at an oxygen or air saturated electrode, (2) inhibition of a hydrocarbon saturated electrode by injected oxygen or air, and (3) inhibition of a hydrocarbon depolarized electrode by extreme polarization. All of these are probably due to adsorbed oxygen or catalytically inactive oxide films, yet they differ in detail. Recovery of electrode activity depends on the removal of the inhibitor. The rate at which this occurs will depend on the nature of the inhibitor but also on the fuel and operating conditions. Some factors affecting electrode potential and inhibition behavior will be discussed in the following section.

a. Nature of Mixed Anode Potentials

Initially, when two electrochemically active species contact different sites on the surface of an electrode, potentials characteristic of the processes involved tend to develop at these two points. This causes electrons to move in the conducting electrode in order to equalize the potential of the electrode surface. If a net transfer of electrons from one species to the other can occur, reactions proceed.

The net anode potential observed will be intermediate between the open-circuit potentials that would be observed for the two reactants separately. Its magnitude will depend on the polarization of the two processes which, in turn, will be determined by the polarizability and effective "current density" as determined by relative surface coverage for each reactant. To a lesser extent, it will depend on the geometry of the electrode, on the way in which the two species are distributed on the surface, and on the location of the connections of the potential-measuring device to the electrode.

From this picture, it is obvious that the coupled oxidation-reduction of a hydrocarbon and oxygen at a platinized electrode in contact with electrolyte can be purely "electrochemical." There need be no direct contact of the reacting species. In this sense this oxidation-reduction differs from direct chemical reaction. It differs also from heterogeneous catalytic oxidation-reduction processes where an electrolyte is not present. These, in general, are believed to require that the reactants contact or at least be adsorbed close to one another. Direct chemical reaction can, of course, also be involved in the electrode recovery process.

   b.   Selective Adsorption and the
        Relative Strengths of Adsorption
        of Reactants and Inhibitors on Platinum

        (1)   Induction Period Due
              to Oxygen Adsorption

Oxygen is known to adsorb rapidly and completely to give a 1:1 ratio of oxygen atoms to surface platinum atoms.[8] On the other hand, coulometric methods show that only about 10% of the surface platinum atoms which will adsorb oxygen are covered with propane at 1 atmosphere pressure in the presence of dilute sulfuric acid electrolytes. Similar coverages are obtained with ethane. Only slightly higher coverages were obtained with ethylene and probably with propylene.[4] Thus, when an electrode is exposed to air or oxygen before contacting with hydrocarbon, the catalyst sites which can catalyze the electrochemical oxidation of propane or propylene are covered. When placed in an electrolyte, this electrode develops the oxygen potential. When propane or propylene is passed through this electrode, the potential is not affected to any extent at first. Gradually, a few molecules of oxygen leave the electrode surface and are removed by the hydrocarbon stream; or they are removed by a catalyzed chemical reduction. This allows the hydrocarbon access to the catalyst sites. The amount of hydrocarbon reacting increases as oxygen is removed; and then suddenly, as the amount of oxygen is reduced to a low level, the hydrocarbon potential resulting from chemisorption becomes dominant; and there is a sudden decrease in net anode potential. After the oxide layer has been removed (approximately 0.55 volt), the potential approaches the open-circuit potential logarithmically with time. The rate is determined by the rate of oxidation of the hydrocarbon and by the capacitance of the ionic double layer.

Following inhibition of this kind (Figure 9), the potential drops below the open-circuit hydrocarbon potential and then gradually rises to the open-circuit potential. This may be due to formation of a particularly active catalyst surface as the oxide film is reduced.

This may survive long enough to dissociate more propane than the usual catalyst, giving a higher hydrogen atom concentration than is normal for the electrode surface.

Behavior after polarization under load to the oxygen potential is very similar to that from oxygen inhibition after standing for several hours in the presence of air and absence of propane (Figure 11). Recovery after polarization and presumably after the other similar inhibition processes can be assisted by injecting hydrogen into the hydrocarbon feed (Figure 12).

Inhibition to the oxygen potential by oxygen injection into a propane stream passing through the electrode does have some different characteristics (Figure 10). This type of inhibition requires a comparatively large amount of oxygen. The propane adsorbed on this electrode must be displaced by oxygen, and this may be a comparatively slow process. More than a monolayer of oxygen may also be retained on the platinum or loosely adsorbed on the graphite. This may result in the more gradual transition to the open-circuit propane potential observed with this system.

If inhibition results from injection of a small amount of air or oxygen which is added to a stream of hydrocarbon passing through an electrode, the effect is immediate because open sites on the catalyst surface are available. If the amount of air or oxygen is not enough to displace all of the hydrocarbon, electrochemical reduction and elimination of the added oxygen begins immediately and hydrocarbon potential is soon established again.

A detailed understanding of the factors which determine the shape, height, and inhibition peak potentials might lead to useful methods for evaluating and studying the behavior of porous electrodes. However, the situation is complex; and more study will be required before complete understanding or useful application of inhibition techniques can be expected.

Acknowledgment

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TABLE I

PREPARATION AND GEOMETRIC AREAS OF SOME PLATINIZED POROUS CARBON ELECTRODES

Electrode	Carbon Base Material*	Geometric Area, cm²	Platinum Solution (H_2PtCl_6) Wt % Pt	Other Components	Method	Number of Times Plated
A	139	29.9	0.5	0.12 N HCl	A	6
B	139	31.8	0.5	0.12 N HCl	A	1
C	139	30.0	0.5		A	2
D	139	30.6	0.5		A	2
E	139	35.4	0.5	0.12 N HCl	A	3
			0.5		A	2
F	FC-14	24.0	0.5	0.12 N HCl	A	1
G	139	33.0	10.0	0.04 wt % Pb Acetate	B	1

* No. 139, Stackpole Carbon Company,
  St. Mary's, Pennsylvania
  No. FC-14, Pure Carbon Company,
  St. Mary's, Pennsylvania

TABLE II

CARBON DIOXIDE PRODUCED BY FUEL CELL OXIDATION OF HYDROCARBONS

Expt. No.	Fuel	Current, ma	Current Density, ma/cm²	Time, hr	Energy, amp-hr	Carbon Dioxide		
						Theory, mg	Found, mg	Per Cent of Theory
1	Propane	25.2	0.84	18.37	0.463	114.2	113.7	99.4
2	Propane	25.2	0.84	18.00	0.453	111.8	112.3	100.5
3	n-Butane	25.2	0.84	6.53	0.169	42.6	45.4	106.6
		10.0	0.33	0.40				
4	n-Butane	25.2	0.84	41.75	1.053	266.0	287.7	108.2
5	n-Butane	25.2	0.84	14.17	0.356	90.3	96.7	107.1
6	Propane	25.2	0.84	14.67	0.369	91.0	90.1	99.0

Propane: $C_3H_8 + 5\ O_2 \longrightarrow 3CO_2 + 4H_2O$ (20-electron change)
$3/20$ mole CO_2 per faraday = 246.5 mg CO_2 per amp-hr.

Butane: $C_4H_{10} + 6\text{-}1/2\ O_2 \longrightarrow 4CO_2 + 5H_2O$ (26-electron change)
$4/26$ mole CO_2 per faraday = 252.7 mg CO_2 per amp-hr.

FIGURE 1

APPARATUS FOR HYDROCARBON PRODUCT STUDIES
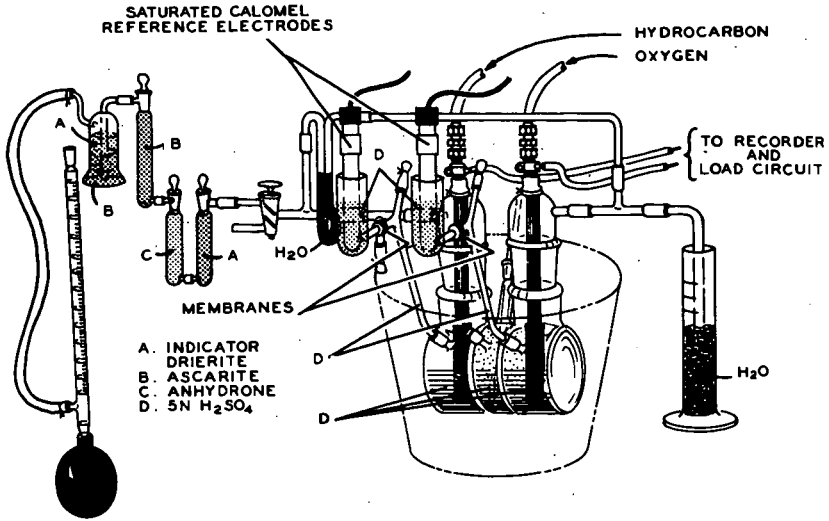
FIGURE 2

PROPANE-OXYGEN FUEL CELL POLARIZATION WITH TIME AS A FUNCTION OF LOAD.
PLATINIZED POROUS CARBON ELECTRODES (TABLE I, ANODE B; CATHODE C)
5N SULFURIC ACID ELECTROLYTE, 80°C
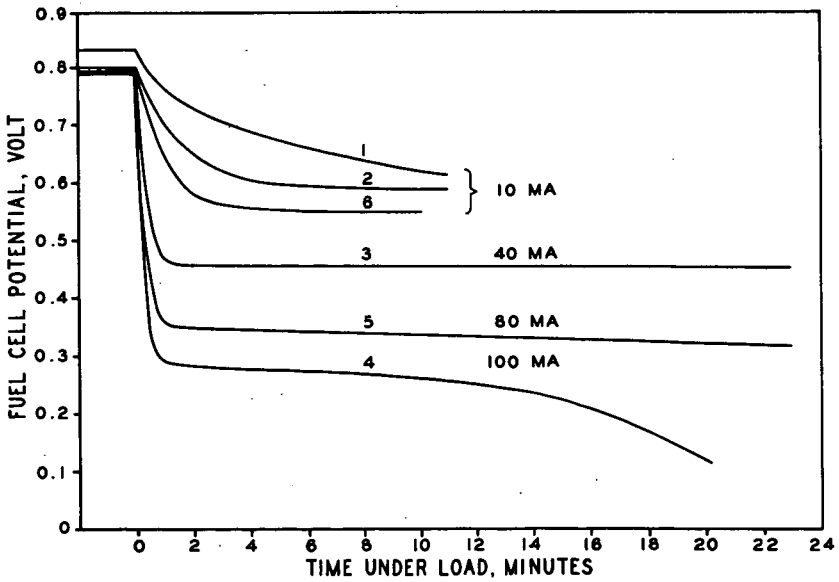
FIGURE 3

FUEL CELL ANODE POLARIZATION DATA WITH PROPANE AT 80°C
PLATINIZED POROUS CARBON ANODE (TABLE I, ELECTRODE C)
5N SULFURIC ACID ELECTROLYTE
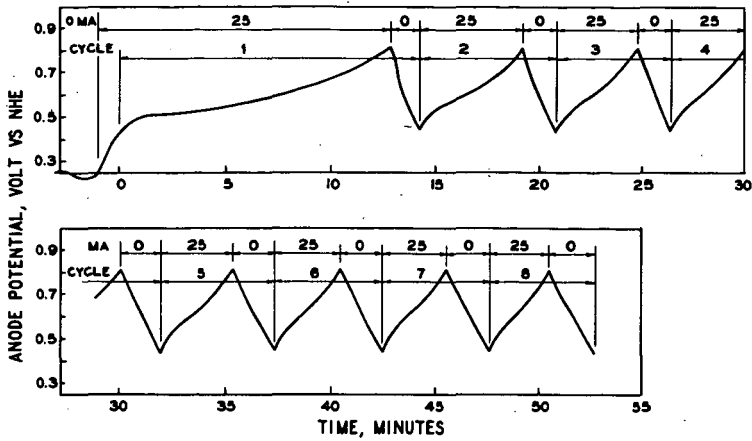
FIGURE 4

THE EFFECT OF THE NUMBER OF LOAD—RECOVERY CYCLES ON POLARIZATION TIME AND
RECOVERY TIME OF A PROPANE DEPOLARIZED ELECTRODE AT 80°C
PLATINIZED POROUS CARBON ANODE (TABLE I, ELECTRODE C)
5N SULFURIC ACID ELECTROLYTE
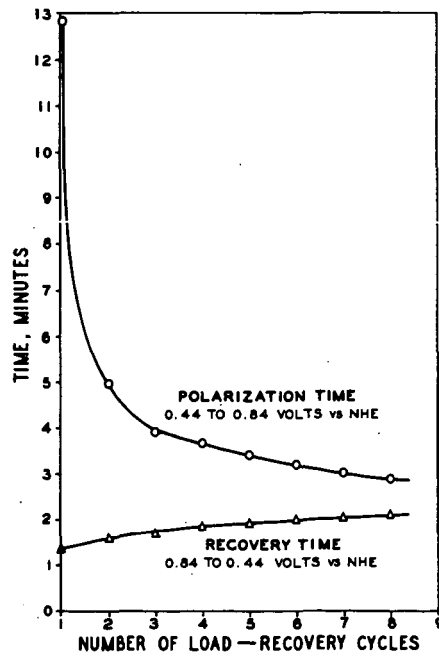
FIGURE 5

CURRENT DECREASE WITH TIME FOR PROPANE-DEPOLARIZED FUEL CELL ANODE AT CONSTANT POTENTIAL
POTENTIAL AUTOMATICALLY CONTROLLED AT 0.74 VOLT VS NHE
PLATINIZED POROUS CARBON ANODE (TABLE I, ELECTRODE D)
5N SULFURIC ACID ELECTROLYTE, 80°C
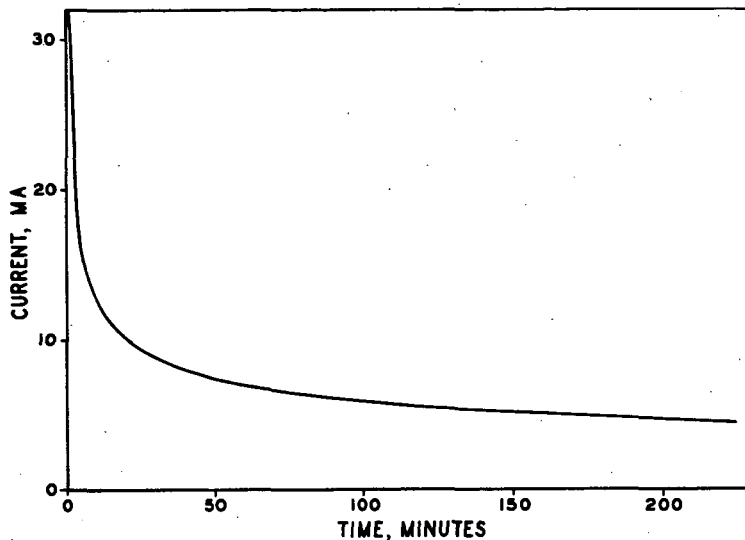
FIGURE 6

THE EFFECT OF ANODE POTENTIALS ON FUEL CELL "STEADY STATE" CURRENT DENSITIES FOR
HYDROGEN, ISOBUTANE, PROPANE AND PROPYLENE
PLATINIZED POROUS CARBON ANODE (TABLE I, ELECTRODE E)
5N SULFURIC ACID ELECTROLYTE, FUEL RATE 10 mL/MINUTE, 80°C

254
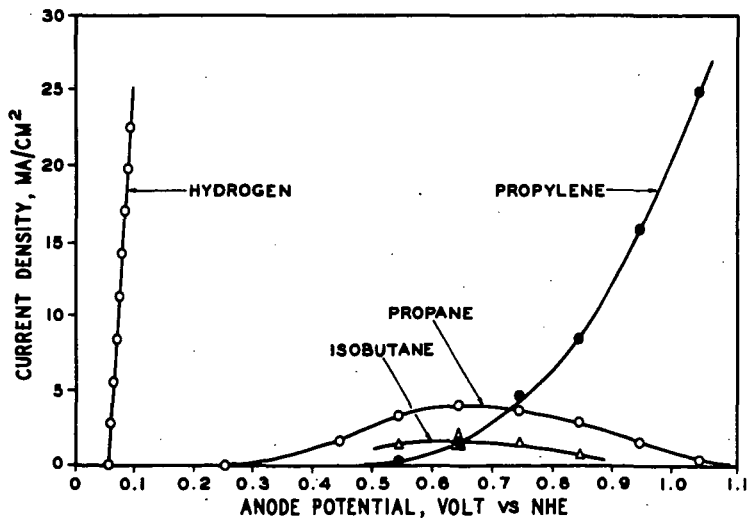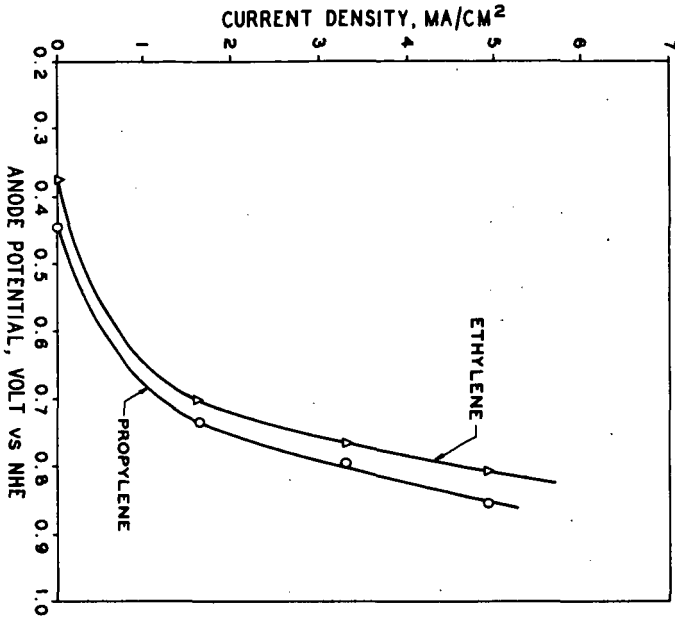
FIGURE 7

THE EFFECT OF ANODE POTENTIALS ON FUEL CELL "STEADY STATE,"
CURRENT DENSITIES FOR ETHYLENE AND PROPYLENE
PLATINIZED POROUS CARBON ANODE (TABLE I, ELECTRODE D)
5N SULFURIC ACID ELECTROLYTE, FUEL RATE 10 ML/MINUTE, 80°C
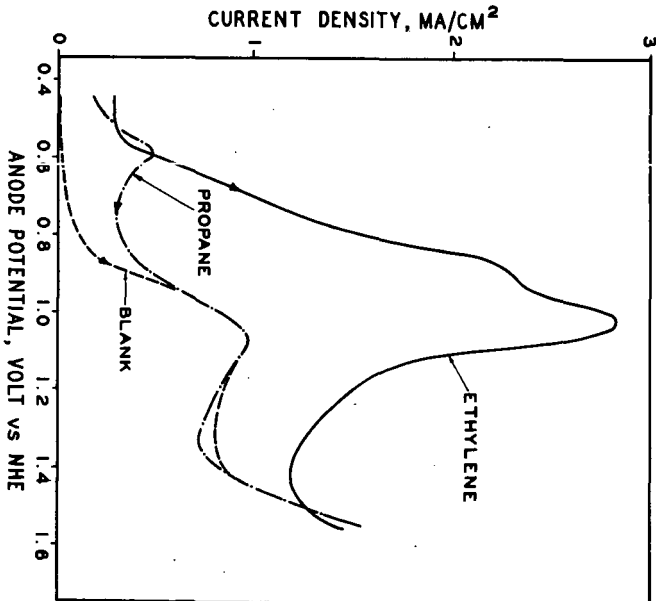
FIGURE 8

CURRENT POTENTIAL CURVES FOR ANODIC OXIDATION OF
PROPANE AND PROPYLENE ON PLATINIZED PLATINUM FOIL
SATURATED SOLUTIONS, 2N SULFURIC ACID ELECTROLYTE,
SWEEP RATE 16.7 MV/SEC, 80°C

FIGURE 9

INDUCTION PERIODS BEFORE ESTABLISHING THE PROPANE OPEN CIRCUIT POTENTIAL OF AN AIR POISONED PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE A) 5N SULFURIC ACID ELECTROLYTE, 80°C
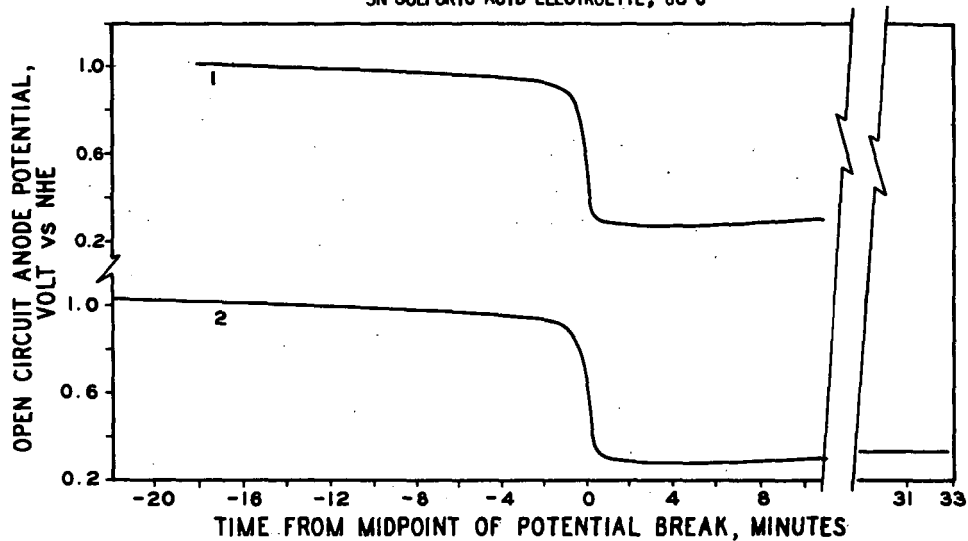
FIGURE 10

OXYGEN INHIBITION OF A PROPANE DEPOLARIZED ELECTRODE PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE F) 1N SULFURIC ACID, 80°C
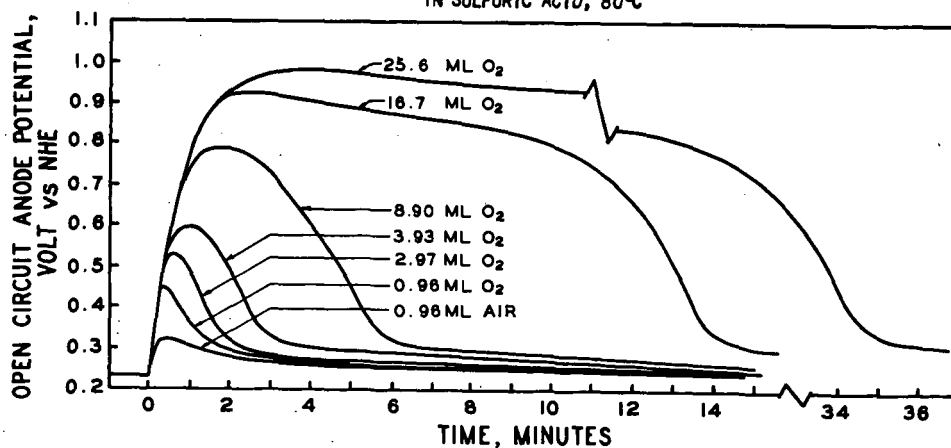
FIGURE 11

EFFECT OF ANODE POTENTIAL OF A PROPANE DEPOLARIZED ANODE ON
RECOVERY AT OPEN CIRCUIT
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE G)
5N SULFURIC ACID ELECTROLYTE, 80°C

AT 0.54 TO 0.94 VOLTS, LOAD ADJUSTED TO MAINTAIN POTENTIAL CONSTANT FOR
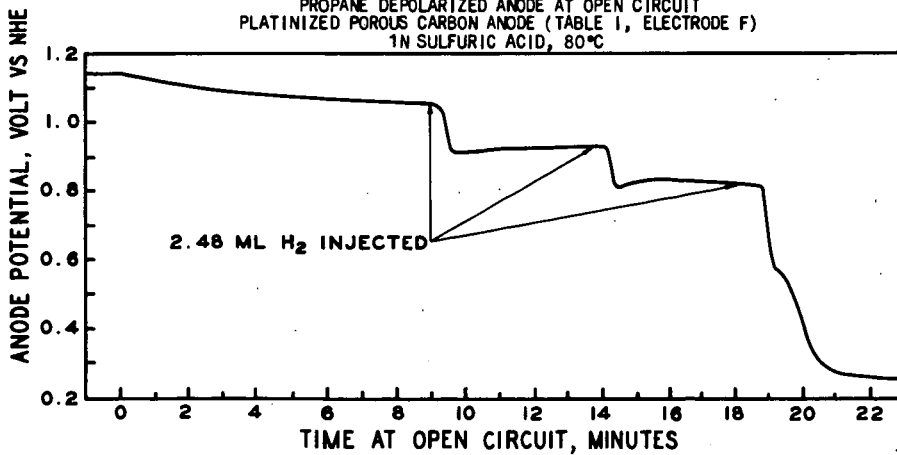7 MINUTES BEFORE RECORDING OPEN-CIRCUIT POTENTIAL

TIME AT OPEN CIRCUIT, MINUTES
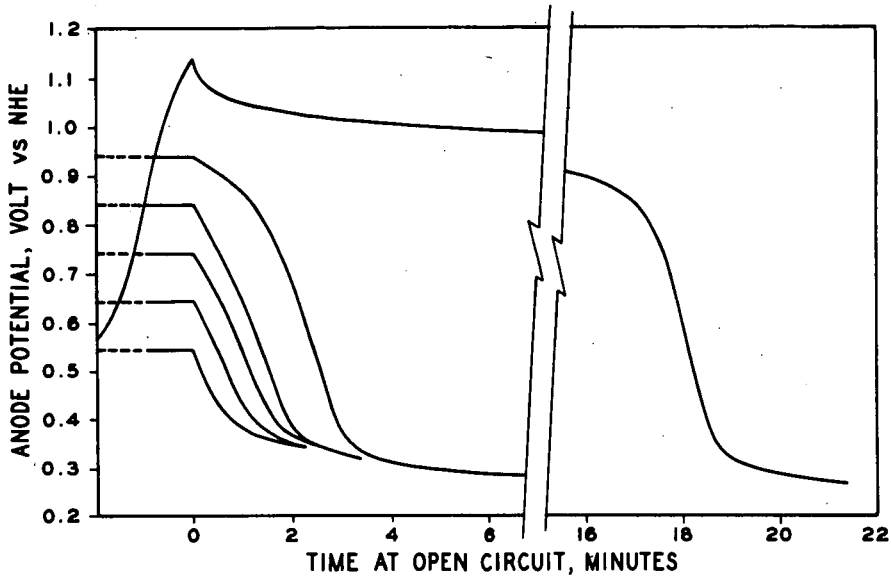
FIGURE 12

EFFECT OF INJECTED HYDROGEN ON THE RECOVERY OF A
PROPANE DEPOLARIZED ANODE AT OPEN CIRCUIT
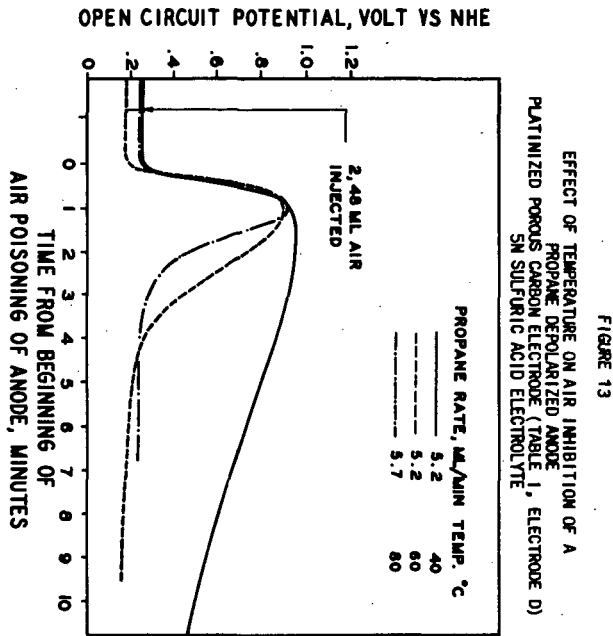PLATINIZED POROUS CARBON ANODE (TABLE I, ELECTRODE F)
1N SULFURIC ACID, 80°C

2.48 ML H$_2$ INJECTED

TIME AT OPEN CIRCUIT, MINUTES

FIGURE 13

EFFECT OF TEMPERATURE ON AIR INHIBITION OF A
PROPANE DEPOLARIZED ANODE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
5N SULFURIC ACID ELECTROLYTE

FIGURE 14

EFFECT OF PROPANE FEED RATE ON AIR INHIBITION OF A
FUEL CELL ANODE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
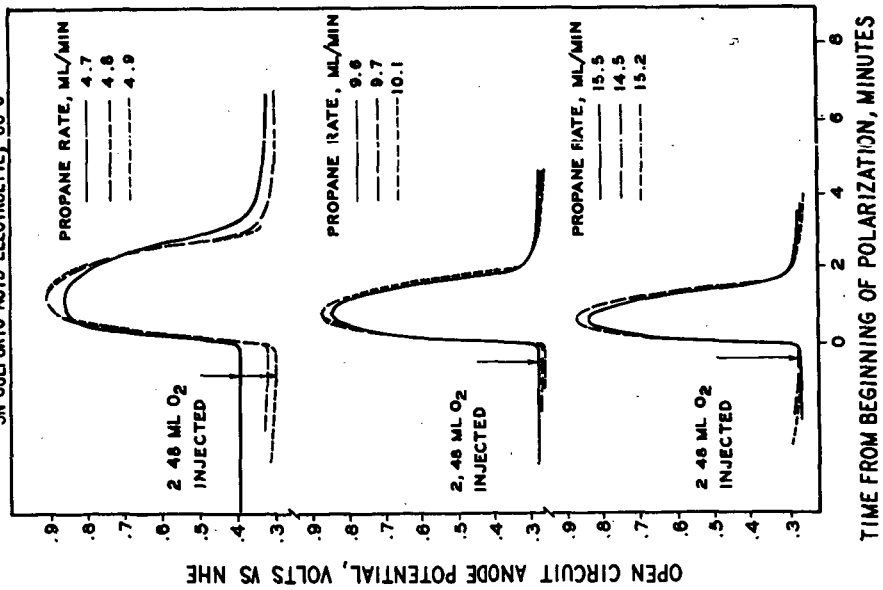5N SULFURIC ACID ELECTROLYTE, 80°C

FIGURE 16

EFFECT OF PROPYLENE FEED RATE ON AIR INHIBITION OF A
FUEL CELL ANODE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
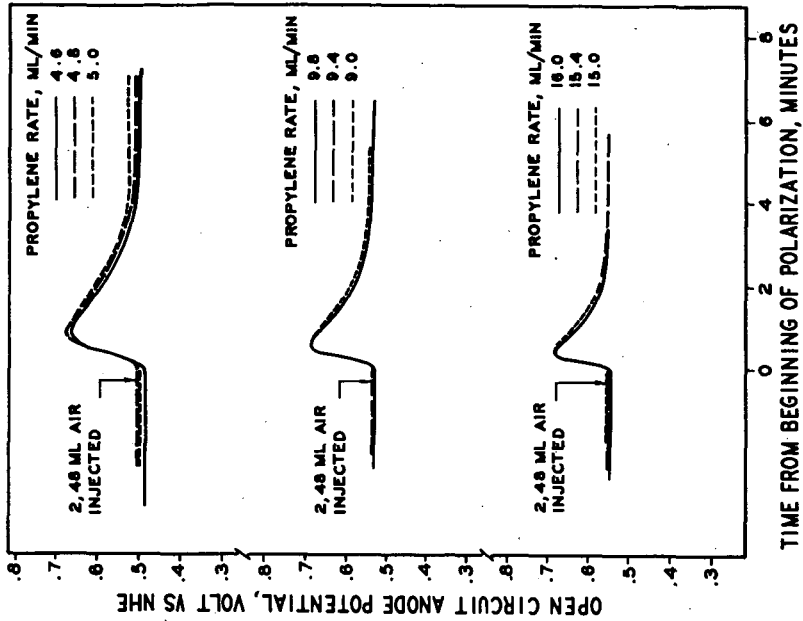5N SULFURIC ACID ELECTROLYTE, 80°C

FIGURE 15

EFFECT OF PROPANE FEED RATE ON AIR INHIBITION OF A
FUEL CELL ANODE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
5N SULFURIC ACID ELECTROLYTE, 80°C

FIGURE 17

EFFECT OF PROPYLENE FEED RATE ON
OXYGEN INHIBITION OF FUEL CELL ANODE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
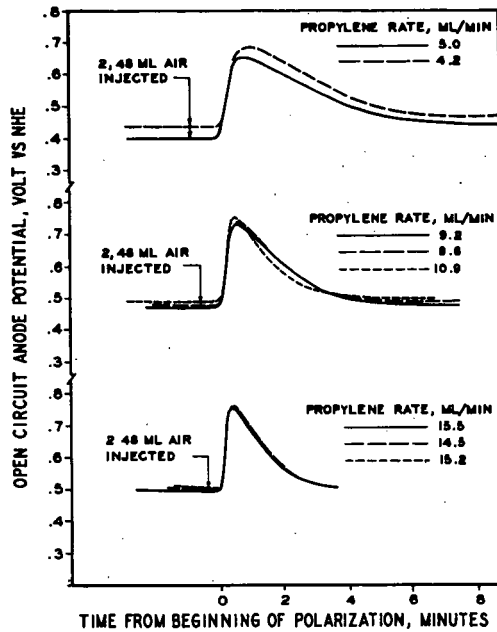5N SULFURIC ACID ELECTROLYTE, 80°C

FIGURE 18

EFFECT OF HYDROCARBON FLOW RATE ON THE RECOVERY TIMES FOR A FUEL CELL ANODE
AFTER INHIBITION WITH AIR OR OXYGEN
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
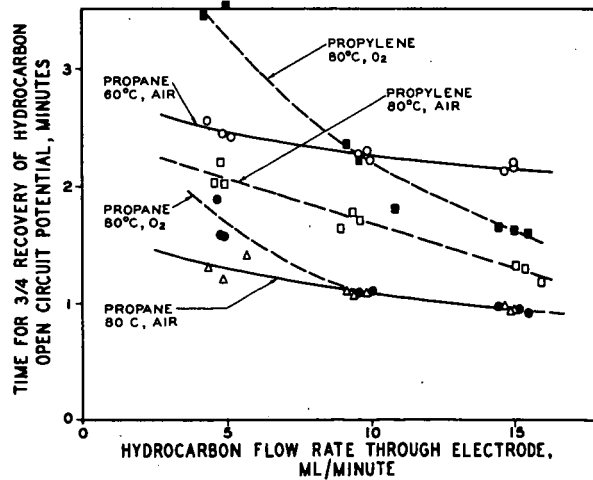5N SULFURIC ACID ELECTROLYTE, 80°C

FIGURE 19

EFFECT OF LOAD CURRENT ON AIR POISONING OF A FUEL CELL ANODE
DEPOLARIZED WITH PROPANE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE D)
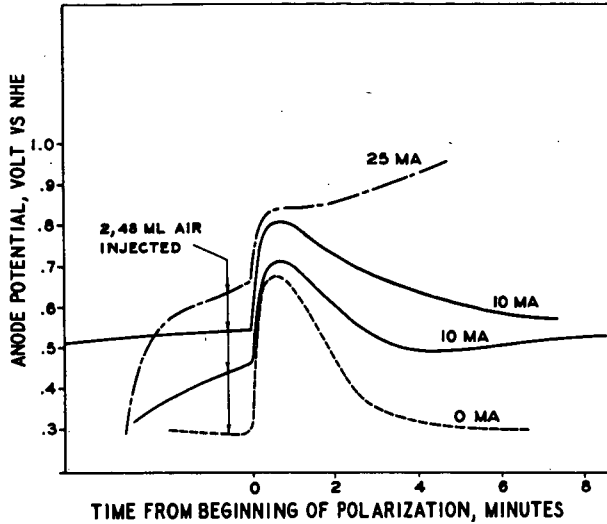5N SULFURIC ACID, 80°C, PROPANE RATE 15 mL/MINUTE

FIGURE 20

EFFECT OF THE AMOUNT OF AIR OR OXYGEN INJECTED ON THE INHIBITION OF
A PROPANE DEPOLARIZED FUEL CELL ANODE
PLATINIZED POROUS CARBON ELECTRODE (TABLE I, ELECTRODE F)
1N SULFURIC ACID ELECTROLYTE, 80°C, PROPANE RATE 10 mL/MINUTE